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EDITORIAL

A New Year's Greeting

WE have already looked back on the departing year and now rather gladly turn to watch the beginning of a new one. The sinuous curve that represents the sun's activity, and indirectly our own, is now reaching a minimum, with the characteristic of all minima, a pause denoted by a brief line of hardly any visible change. Our short vacation coincides with the winter solstice and when, on Sunday afternoon, we reflect on the tempestuous year and discover that at last all is calm and that we may sleep in port, we shall be gladdened by the thought that already the day is lengthening and that before long the increased power of the sun will by heavenly alchemy produce leaves green with substances and formulæ that we may ignore for the moment. In these climes the days will soon be bright and cheerful; in some of the countries far in the north, there are no days now, only gloomy intervals between bitter nights: even there the snow melts at last and with what extraordinary rapidity do the herbs and trees make up for lost time! We have many hopes for the New Year. We hope that our Chancellor's expectation of a good budget surplus will be realized and that there may be some mitigation of the present burden of taxation; let there be more men and women employed in industry and fewer chemists looking for a post and thankful when at last they obtain a remuneration which would not satisfy a dustman. We are already moving steadily along the road to prosperity, and goodwill, and hardly dare to hope for more than progress along this path. We trust that in the United States there will soon be a hopeful result from one of the many experiments they are making there, a result that will justify them in hastening the procedure indicated and speedily lead them towards prosperity. It is singular that the great nations know so little about the causes of prosperity, though we should hardly expect them to know as much as an intelligent individual who spent a little time studying the problem. To all our friends in the Empire on the continent of Europe, and elsewhere, we wish prosperity, and goodwill, and peace. We not only wish these: we hope for them very confidently. These three will to some extent go together; in Germany we hope that industrial conditions and unemployment will improve to such an extent that Germany can take a less desperate and more broad-minded view of her neighbours, her creditors, and those at present exiled from their native land. We do not easily know the true state of German opinion for only one variety of opinion is permitted in Germany and no government can be as truthful as a conscientious individual. No squadron of cavalry can move at the speed of a single trooper and if you have a bundle of sticks, or opinions, the tighter you bind them together the more you distort and strain them. Freedom of thought and of speech were once highly valued, perhaps too highly valued: that sort of freedom has had some terrible blows in more than one country in Europe but it is not yet killed:

Thy tree hath lost its blossoms, and the rind,
Chopp'd by the axe, looks rough and little worth,
But the sap lasts, and still the seed we find
Sown deep, even in the bosom of the North;
So shall a better spring less bitter fruit bring forth.

The desire for uniformity in every sphere of life is perhaps brought about by a general sense of dissatisfaction, but it does not prevail very greatly in this sceptred isle and anything that resembles a religious persecution seems to us rather unjust. The revocation of the Edict of Nantes was perhaps considered at the time a necessary precaution but it has ceased long ago to be an example to be admired. We trust that chemists—and the same applies to most intellectual workers—will continue in all countries to work carefully and fearlessly and to work cordially and harmoniously with the chemists of other nations and other creeds so that chemistry may be a bond binding together by mutual goodwill those whose lives are spent in the advancement of knowledge and its application to the prosperity of mankind. We trust that such a devotion to truth and civilization may act as an enzyme stimulating a far larger mass towards a higher and nobler aspect of life, and that the international sense of chemistry will produce good results when chemists meet together in Madrid next April. So far as this JOURNAL is concerned we expect to receive as many excellent papers in 1934 as we did in 1933 and that our pages will continue to grow in number and value. A comparison of our JOURNAL of this time with that of forty years ago shows a very great advance and there appears to be no reason to think that we have reached a limit. For our Society we wish the same public-spirited devotion on the part of our members as has long distinguished them: we desire the same quality and rather larger numbers, and to all our members, contributors, and readers we wish every good fortune during the year that is to come.

The Bergius Process for the Production of Sugar from Wood

We publish this week an interesting paper by Dr. Bergius read before the Institution of Chemical Engineers on the saccharification of wood. This process was described by Dr. Ormandy in these columns (J.S.C.I., Aug. 13, 1926, 267 T) some years ago and in the intervening time the process has been developed and improved. If it is now in the stage when it is profitable it will make many changes in the geographical distribution of sugar factories and in the nature of export trade. Foreign trade has always been a very changing one, as new discoveries of countries, natural products, and raw materials have been made. There was a time when we exported tin from this country; we now import tin from the Malay States and Bolivia. There was a time when we exported wool from this country to Flanders to be manufactured in Ypres and other towns. Formerly we imported indigo from India and madder from the Mediterranean; fifty years ago the Germans were engaged on the synthesis of indigo and synthetic indigo has now displaced the natural product and is exported from this country. Many such instances could be given; in some cases the change involves very little disturbance in the volume of international trade, only in its character or direction; in other cases the volume of trade was seriously diminished. Thirty years ago we imported great quantities of pig lead from Australia, converted it into white lead and red lead in this country, and shipped these back to Australia. Now the Australians make their own white lead and red lead and lead paints from their own lead in their own country. The papyrus was in old times almost the only material suitable for writing and the manufacture of it was confined to Egypt. Paper can be made in almost any country but particularly in those countries where wood and water power are plentiful. Textile threads and yarns can now be manufactured in any country sufficiently civilized to train up chemists, and ammonia and nitrates can be made in any country in which there are chemists and nitrogen. When the manufacture of sugar from wood is sufficiently lucrative one might expect it to prevail where wood is plentiful and land is cheap. The distressed Newfoundland may find employment for some of her impecunious inhabitants and sugar factories may be erected even nearer home than that. When the Bergius process is working vigorously we may find that it will be a valuable assistant to the distillers. Perhaps in the future the motorist or airman taking a holiday in Scotland will find sugar factories in Mull, and Skye, and on the banks of the Spey. The new use of wood may stimulate our Forestry Commissioners to even greater activity and the development of woods and forests should proceed apace, for some day an ingenious man will invent a synthetic process for the manufacture of alcohol and another process for converting alcohol into sugar, and new industries will spring up in new countries and so the changes will go on for ever.

The Chemistry of Cooking

This is the season in which the chemist may cast his cares aside and lightly turn to thoughts of food. Food—of a kind—has, it is true, been much in the Society's mind during the last month, but we venture to doubt whether a Christmas fare of milk and bread would appeal even to those who so ardently supported these necessary foodstuffs at the recent Food Symposium. At the moment they would probably prefer to discuss port and turkey and their palatability rather than their vitamin content. We recommend as seasonable literature the latest report issued by the Medical Research Council on The Chemistry of Flesh Foods and their Losses on Cooking, by Dr. McCance and Mr. Shipp. This fills a very large gap in our knowledge of nutrition, for not only have the compositions of a great many foods, especially fish, been investigated for the first time, but the authors have approached their subject from a different angle than usual, that of the consumer and not of the butcher or fishmonger. They have analysed the foods after cooking and not before and also shown the differences in the composition of the same substance after different methods of cooking. These differences are larger than one realizes. For instance fried fish contains, on an average, six per cent. more carbohydrate and ten per cent. more fat than boiled fish and also more of the elements sodium, chlorine, and iron. The reason for this is very simple; the carbohydrate comes from the added breadcrumbs, the fat from the butter or lard, the sodium and chlorine are the constituents of the added table salt, and the iron is provided by the frying pan. This is the first occasion on which we have regarded frying pans as nutritious. The authors have not attempted to discuss the palatability or otherwise of the various foods, but they have had to consider how much of the food is edible; the skin of fish and the fat of meat, for example, while highly esteemed by some, may yet be spurned and pushed aside by the more dainty feeders. We note that the tail of the sardine is considered edible but not the backbone, the sprat on the other hand has to have its head removed before it is eaten, while the whitebait is completely devoured. These three fish have a high dietetic importance as valuable sources of calcium and phosphorus, owing to the large number of small bones they contain which are necessarily eaten with them. The larger part of the report is devoted to a study of the losses on the cooking of fish or meat and a comparison of the losses on different methods of cooking. The authors discuss the analytical methods they have used and compare their methods with those of earlier workers. The descriptions of their analyses are very detailed and could very easily be followed by anyone wishing to repeat them. The whole report has been very carefully written and the work should serve as a model of what an accurate piece of research should be. The Medical Research Council are to be congratulated on the addition of this report to an already very adequate series.

THE UTILIZATION OF WOOD FOR THE PRODUCTION OF FOODSTUFFS, ALCOHOL, AND GLUCOSE

By DR. FRIEDRICH BERGIUS

Paper read before the Institution of Chemical Engineers, on Wednesday, Nov. 15, 1933

At a joint meeting of a number of chemical societies and institutions in London in July, 1926, Dr. W. R. Ormandy delivered a lecture on the production of sugar from wood. In this lecture he referred to the process of saccharification of wood, which has been developed by my collaborators and myself during the last fifteen years. It is now a great pleasure to me to have this opportunity of describing to you the steps by which we have developed the process up to a commercial scale in our works at Mannheim-Rheinau.

In the first place I should like to give a short historical review of the subject of the saccharification of wood.

For more than a hundred years it has been known that the cellulosic constituents of wood can be converted into fermentable carbohydrates by relatively simple means. The saccharification of starch, accomplished by Kirchhoff at Petersburg in 1811 by means of dilute acid, must be considered as a forerunner to saccharifying wood. The first attempts to saccharify wood were begun only a few years later. Braconnot observed in 1819 that the cellulose which was digestible only by bacteria could be converted into various forms of sugar by treating it with concentrated sulphuric acid. In 1855 Melsens used dilute hydrochloric acid of from 3% to 5% strength as a means of disintegrating wood shavings, while Béchamp a year later used concentrated sulphuric acid for the saccharification of wood. All these and similar other experiments, however, did not result in an industrial solution of the problem.

Attempts to saccharify wood on an industrial scale were instituted at the beginning of this century on the basis of converting wood into sugar solution by means of dilute acids under heat treatment, from which solution alcohol was to be made by fermentation.

The first technical plant for the production of alcohol from wood was established in the United States in 1910 by Ewen and Tomlinson, and used waste shavings from a saw mill in Georgetown, South Carolina, as the raw material, and dilute sulphuric acid as the saccharification medium. Owing to the low yields (6·5 litres of alcohol from 100 kilos of dry wood substance) this plant proved uneconomic, and was only operated for a few years. Later attempts in the United States to carry out the saccharification of wood on a large scale by dilute acids also proved unsuccessful.

In Germany the problem of producing alcohol from wood assumed importance during the war. In 1916 a plant to use the process of Alexander Classen was erected in Monheim, near Düsseldorf, and later another plant at Stettin. Here mixtures of dilute hydrochloric acid, sulphuric acid, and sulphurous acid were used as disintegrating media. Although the yields were very little greater than those obtained in the American plant, nevertheless the quantities of alcohol recovered were of importance owing to the abnormal conditions obtaining during that period. The large consumption of wood and the correspondingly high operating costs did not play a decisive part during this time.

An improvement over these methods of producing alcohol from wood with dilute acids was brought about a few years ago by the Scholler-Tornesch method, and, a short time later, by the Epsom process. These processes use dilute sulphuric acid of 0·2% to 0·8% at temperatures of from 160° to 190° C. under a pressure of about 10 atm. Scholler obtained from 60% to 70% of the theoretical yield, that is, 20 to 24 litres of alcohol per 100 kilos of dry wood substance by his method. However, since the solutions contain only 2% to 3% sugar, they can only be used for conversion into alcohol or other products of fermentation. The economical production of a solid or highly concentrated carbohydrate is not possible in this way as the quantity of liquid to be evaporated is too great.

These processes bring about the transformation of cellulose into sugar by a dilute acid at relatively high temperatures. At the temperature necessary for the reaction, the glucose formed from the cellulose is not stable and is easily decomposed. The percentage of decomposed cellulose was very high in the processes of Ewen and Tomlinson and Classen. It was brought down considerably in the Scholler and Epsom processes. This increase in the percentage of sugar produced from the wood, however, could only be obtained by decreasing the sugar content of the final solutions. These processes make use of the fact that the decomposition of sugar is smaller in a weak than in a highly concentrated solution. Obviously the decomposition of sugar cannot be avoided, and 30% to 40% of the wood sugar is lost during the operation.

This loss can be avoided if the hydrolysis of the cellulose is conducted at temperatures at which glucose is stable in the presence of acid, but for the

action on cellulose at low temperatures a relatively strong and concentrated acid is necessary.

By using concentrated sulphuric acid Ost showed, as early as 1910, that practically the whole of the cellulose could be recovered in the form of glucose. This method, though workable on the laboratory scale, cannot be employed industrially because a considerable quantity of sulphuric acid is necessary for the reaction, and no way has yet been found to separate and recover the sulphuric acid from the glucose. Such a process is naturally economically impossible unless methods are developed of recovering the acid.

In 1910 Willstätter and Zechmeister published the well-known paper in which they stated that, at *normal temperatures, hydrochloric acid* containing at least 40% of HCl easily dissolves cellulose with the formation of a glucose solution.

In 1916 the conditions in Germany, brought about by the war, made it impossible to import foodstuffs, and it became evident even to the most zealous free trader that the home production of foodstuffs, and especially carbohydrates, which are more or less the basis of every foodstuff, was of fundamental importance for the life of the nation.

Every year on every acre of forest land nearly *the same quantity of digestible cellulose and other* carbohydrates is produced as on an acre of land under oats, and, further, only about 50% of the available wood can be used as timber, the other 50% being burned or wasted. It therefore became obvious that there was an enormous source of raw material for the production of foodstuffs at the disposal of mankind if a technical process could be found to effect the transformation of the carbohydrate content of the wood into glucose or similar digestible carbohydrates.

These reflexions encouraged us to take up the problem of the saccharification of wood. The question of making alcohol from wood was, from our point of view, a problem of minor importance which *obviously could be solved simultaneously*. Our problem was to produce a concentrated and digestible sugar or a mixture of sugars which could be used as human food directly in the form of pure glucose or indirectly in the form of a carbohydrate cattle food. The question of procuring protein might also be solved at the same time. The production of yeast from glucose by using ammonia as source of nitrogen has ceased to be a problem.

Willstätter and Zechmeister's method of reaction by means of concentrated hydrochloric acid seemed the best possible basis for a technical process. The velocity of the reaction between hyrochloric acid and cellulose is sufficiently great at normal temperatures when hydrochloric acid is brought into contact with dry wood. *The solution containing 2/3 of the* dry wood substance may easily be separated from the remaining part of the wood, the lignin. The most difficult problem was the separation of the relatively large quantity of hydrochloric acid from the sugar solution, so that, first of all, we had to devise a reasonable method *for recovering the hydrochloric acid* by vacuum distillation.

In 1916 we began to build up the wood hydrolysis process, sometimes called the "Bergius Wood-Sugar Process," under the auspices of Th. Goldschmidt A.G., Essen, but this process is not based on one fundamental invention made by myself, but is the result of collaboration of a number of chemists and engineers who were, for years, working with me and under my direction. Of these members of our organization I want to mention the names of Prof. *Erik Hägglund and Fritz Koch*, who have been working on these problems from the beginning, and E. Färber, who joined our organization a few years later.

The reaction between wood and *hydrochloric* acid of 40% strength requires a comparatively large surplus of acid. To produce the largest possible quantity of sugar from the wood, 7 parts of hydrochloric acid have to be added to 1 part of wood. In this way a solution is obtained containing less than 10% of sugar. The recovery of the hydrochloric acid from a solution containing only 10% of sugar would be a difficult and expensive procedure. It was found, however, that a sugar-containing solution is able to react with fresh wood, thereby *increasing its concentration of sugar*. Ultimately an equilibrium between the hydrochloric acid and the cellulose is attained.

Making use of this fact, we succeeded in increasing the sugar concentration by conducting the process in a battery of from 8 to 10 vessels. The fresh wood filled into vessel No. 1 is brought into contact with an acid containing a comparatively high concentration of sugar coming from vessel No. 2. Vessel 2 contains wood which has already lost part of its cellulose content and is now brought into contact with the solution coming from vessel 3 and so on. The last vessel of the battery is filled with the highly concentrated acid which dissolves the last traces of the cellulose material and leaves a lignin free from *both cellulose and sugar*. With this method we were able to increase the sugar concentration up to 40%, which is obviously of enormous advantage in the recovery of the hydrochloric acid in the next stage of the process. The last vessel filled with lignin and hydrochloric acid free from sugar is now washed out systematically with the minimum amount of water. The acid from the washing treatment is then conveyed to a plant where hydrochloric acid gas is added to increase the HCl concentration to 40%, so that the acid can be used again for a new operation. After this systematic washing the lignin contains only very small traces of hydrochloric acid which can easily be washed out with water, and the lignin removed from the vessel. When opening the latter at its lower end, the lignin falls out and, being completely free from acid, it can be handled and transported by normal means.

This battery of vessels is the only part of the wood sugar plant where a *chemical reaction* takes place. But this reaction is not as simple as it would

seem at first sight. It is not only the cellulose of the wood which is attacked and hydrolysed by the acid, but the hemi-cellulose, hexoses, and pentoses are likewise easily dissolved.

Acetic acid is found in the sugar solution in about the same quantity as is obtained by the wood distillation process. It constitutes an interesting by-product of the process.

The reaction between dry wood and hydrochloric acid is exothermic. The heat produced during the operation is derived from two sources: dry wood develops heat when it comes into contact with water, and the hydrolysing reaction also produces a certain quantity of heat. If, in carrying out the process on a large scale, means were not provided to prevent increase of temperature, great loss of sugar would occur which would render a technical procedure impossible. The relatively large quantity of liquid acting on the wood is a very good medium for avoiding superheating if from the beginning of the reaction measures be taken to ensure that every part of the fresh wood comes in direct contact with the liquid. For this purpose, the fresh wood, before entering the reaction vessel, is mixed with the liquid on a special conveyor.

The final product from the batteries consists of a solution of sugar in concentrated hydrochloric acid, and means had to be devised to separate the sugar from the acid, employing relatively low temperatures, that is 40° and 50° C., to avoid decomposition of the sugar, and to maintain the acid in the concentrated form. It is important that the resulting sugar should contain only minimum quantities of acid, as any residual acid would impair the usefulness of the product. The method finally devised depended on vacuum distillation, and it is an advantage of this method that the hydrochloric acid is volatile at relatively low temperatures. Such a method presents no difficulty in a laboratory apparatus made of glass, but it becomes complicated when conducting it on a large scale. When we began our work, no method existed for the distillation of hydrochloric acid in large quantities. All normal materials used in the construction of distillation plants do not resist concentrated hydrochloric acid. The only metal which might be used is tantal, but the cost is prohibitive. The stone-ware available at the time had a very low heat conductivity, so it was not possible to build distilling apparatus with stone-ware tubes. Therefore, a special method had to be worked out which avoided the difficulty of transferring the heat necessary for evaporation through the walls of the vessel. We used the principle of transferring the heat directly by a fluid heat conductor to the solution to be distilled. A petroleum fraction which remains fluid at the working temperature is used as a heat conductor. The solution containing hydrochloric acid and sugar which has been drawn off from the diffuser is introduced into a vacuum apparatus at a temperature which does not incur any appreciable loss of sugar, and is there brought into intimate contact with the oil which serves as a heat carrier. An immediate evaporation of the largest part of the hydrochloric acid takes place, while at the same time a solution is formed with about 60% of sugar, still containing from 8% to 9% of hydrochloric acid. The oil used as heat carrier is easily separated from the concentrated sugar solution and, after being re-heated in a normal steel coil at a temperature of about 100° C., re-enters the vacuum apparatus which runs continuously. This method worked very well and gave the first possibility of solving the problem of the separation of the sugar from the hydrochloric acid. To-day, stone-ware tubes are produced with a much higher heat conductivity, and special vacuum stills, which are working very well, have been constructed of this material.

As no other process existed at the time for the separation of hydrochloric acid from a sugar solution, the evaporation method, using oil, played an important part in the development of the whole process. This vacuum evaporation, however, does not suffice for the complete removal of the hydrochloric acid. The concentrated syrup still contains 8% to 9% of the acid, which means 40% to 50% calculated on the sugar. It is impossible to remove the remaining acid by a normal concentrating or drying method. Only by treating this syrup with hot air in a special atomizing-drier in which it is finely atomized by air pressure and dried in a stream of hot air can the hydrochloric acid content be brought down to 1% to 2%. The hydrochloric acid thus removed is available for further use in the process.

The product leaving the drying apparatus contains about 90% of sugars of different kinds, and about 2% of hydrochloric acid, as well as small percentages of other organic and inorganic substances and water. This product, a raw wood sugar, is the final product of the primary process. The distillate from the vacuum still also contains the acetic acid formed during the process. A special method was worked out to recover this acetic acid, the output of which is between 3% and 5% when saccharifying conifers, and somewhat higher when treating wood of foliaceous trees. The recovery is effected by a simple method in which the solution is divided into gaseous hydrochloric acid and dilute acetic acid free from hydrochloric acid. The acetic acid can be concentrated under normal conditions.

If the process is conducted in a completely acid-resisting apparatus, and only in such an apparatus can a process like this possibly be carried through, then the losses in hydrochloric acid which are apt to occur are limited to:—

(1) The acid lost when lignin is washed out for the last time;

(2) The acid contained in the raw sugar: and

(3) The small quantity which is lost when concentrating the acid up to 40%.

According to our experience the total loss is not more than 10% HCl calculated on the sugar produced, but we hope to obtain still better results in the future.

Practically no loss of sugar occurs during the reaction, as every possibility of decomposition due to *increase of temperature is excluded.* So when the process is conducted in the right way, the yield in products reaches wellnigh the theoretical output of sugar from wood, that is 66% of the dry wood.

Some years were necessary to build up the chemical basis of the process and to work out a semi-technical *plant in which to test the results of the laboratory* experiments. These latter experiments were carried out on an apparatus which was a real model of a big plant with a battery of 10 vessels, each of 100 litres capacity, and every other detail of corresponding size.

The results of this model plant at Mannheim-Rheinau, constructed and operated between 1920 and 1924, were able to be reproduced between 1925 and 1928 in the first technical plant at Geneva, where the size of the diffusers (Fig. 1) was increased from 100 to 4000 litres, an extraordinarily large advance.

At the Geneva works we first worked on the Prodor process based on the patents of Levy and Terrisse. This process used hydrochloric acid gas in a complicated apparatus for the saccharification of wood, but it proved unsuccessful on the technical scale.

After the failure of the Prodor process we began in 1925 to build up our own process, and after two years of hard work in building, changing, and reconstructing the apparatus, we were able to run this technical plant of intermediate size with satisfactory results. Continuous running demonstrated the fact that the plant was absolutely hydrochloric acid-tight, and this is one of the main requirements for carrying out the saccharification process on the

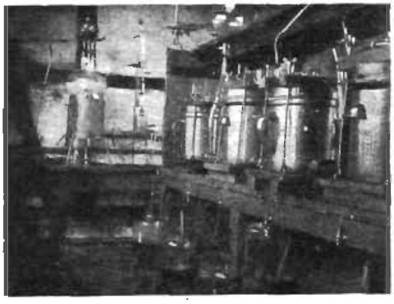

Fig. 1

technical scale, as it demonstrated the flawless operation of the complicated system of piping. Frequent tests made by the local authorities showed that no public annoyance was caused by the hydrochloric acid in the operation of the apparatus, and that there was no trace of hydrochloric acid in the air surrounding the factory. The output of the plant corresponded to the size of the equipment. The yield from the wood in the larger Geneva plant even exceeded somewhat that obtained at Rheinau; also

Fig. 2

the sugar concentrations of the solutions somewhat exceeded those obtained in the smaller plant. The object of the Geneva plant was to determine the technical foundations for the building of wood-saccharification plants, to determine the ratio between the raw materials, the final product, the energy, and to acquaint the staff with the operation of the equipment. For reasons arising from location and organization a further enlargement of the Geneva plant was not considered advisable.

In 1928 the technical staff was therefore taken back to Mannheim-Rheinau to take up the work preparatory to the building of a plant on an industrial scale. In the meanwhile we occupied ourselves there with the questions of procuring wood, the practical uses and the further development of the products. At the same time, the constructional foundations and the cost calculations were made for the transfer of the wood hydrolysis process to a large industrial scale.

Mannheim-Rheinau was selected as a site for the first large factory, because it is situated on a waterway, thus facilitating the transport of the raw materials and of the products. Further, the factory, which was formerly used for our coal hydrogenation process, could be adapted to the new purpose of wood saccharification.

The actual construction began in the autumn of 1932, and by May, 1933, the factory was completed and has now been in continuous operation for some months. Already, it has been shown that the same yield of carbohydrates from wood can be obtained, as in the Geneva plant. The principles underlying the construction of the new large plant are the same as those of the Geneva plant. The large Rheinau plant has a diffusion battery capable of a yearly

production of from 6000 to 8000 tons of pure carbohydrates. The plant can be enlarged simply by the addition of more units. The size of the diffusers is five times that of each diffuser of the Geneva plant, that is, 20 cb. m., or about 700 cb. ft., but whereas the Geneva diffusers were built of acid-resisting Prodorite, the Rheinau diffusers are of iron, lined with small acid-resisting tiles joined together by a special cement. Fig. 2 shows one of the Rheinau diffusers before installation. The mobile wood carrier bringing the raw material to the upper part of the diffusers is shown in Fig. 3.

The wood, which normally contains from 20 to 40% moisture, is first cut, in special shredders and mills, into suitable pieces the size of a kernel of corn, and is then dried in a revolving drier until it contains about 1% of moisture. The heat for drying the wood can easily be furnished by the waste heat of the boilers. Before being introduced into the diffusers, the dry wood is moistened with a solution coming from the last diffuser containing sugar and hydrochloric acid. This is done in the fore-masher from which the mixture of wood and acid is transported to the diffuser No. 1 and dropped in through the top opening.

After allowing a short time for the reaction to take place in this newly filled diffuser No. 1, fresh highly concentrated hydrochloric acid is pumped into the last diffuser No. 8. The liquid contained in this diffuser is then transported to diffuser No. 7, the solution from No. 7 to No. 6, and so on. The solution at the top of diffuser No. 1, containing normally about 35% of sugar, is drawn off to the distillation plant, and a new filling operation may then be started.

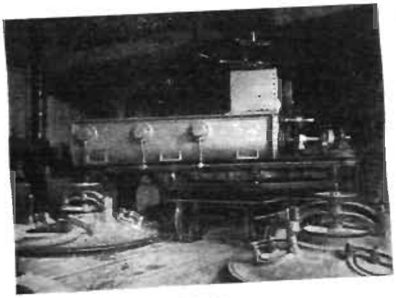

Fig. 3

The vessel No. 8 is washed out systematically, giving a solution with from 37% to 38% of hydrochloric acid, which is then led to the regeneration plant. In the Geneva plant, details of which have already been given by Dr. Ormandy before this [illegible] had a special battery for washing the lignin. To-day we use one of the diffusers for this purpose, which is an important improvement.

The recuperation of the 40% hydrochloric acid is performed by the absorption of HCl gas by the acid from the washing process, and takes place in a plant

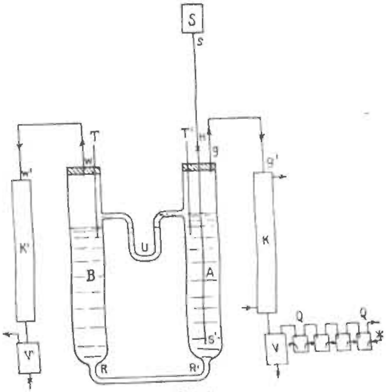

Fig. 4

especially constructed for the purpose. Special means of cooling are necessary to remove the heat generated in recuperating the acid and to keep the acid plant within reasonable dimensions. There is no perceptible smell of acid during the normal running of the plant when producing 40% hydrochloric acid.

In the evaporation station the hydrochloric acid is distilled under a vacuum of about 30 mm. of mercury at temperatures of from 40 to 45° C. We are now working with an apparatus containing 35 tubes of 2 m. length, and a new one is being built which will contain a hundred such tubes. The first apparatus allows a production of 2 tons of sugar a day from a 35% solution, the larger one will increase the production to 6 tons, quite a considerable amount for this simple and comparatively small apparatus.

The iron parts of the evaporator which come in contact with the hydrochloric acid are covered with rubber of a special make. These rubber covers have proved very satisfactory in their resistance to the attacks of the highly concentrated hydrochloric acid under the conditions of the process over many years of practical use.

Condensation of the acid vapours is effected in stone-ware coils which, however, will shortly be replaced by another type of condenser built of protected iron. The small quantity of hydrochloric acid gas which is not condensed is absorbed by the dilute hydrochloric acid, and in this way the vacuum pump is protected against attack by the acid. The

condensates are returned to the recuperation plant and re-used in the process.

At the same time, the acetic acid originating from the wood and contained in the battery solution is distilled and condensed together with the hydrochloric acid. When the concentration of the acetic acid in the condensate reaches 10%, part of the condensate must be removed and the hydrochloric acid separated from the acetic acid. We succeeded in finding a good technical method for this separation, which is illustrated in Fig. 4.

A U-tube is filled with a concentrated solution of calcium chloride of a definite high concentration.

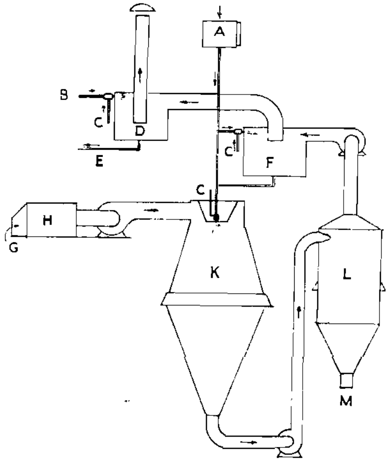

Fig. 5

Zulauf der Zuckerlosung = A. Inlet of sugar solution.
Wasser = B. Water inlet.
Pressluft = C. Compressed air inlet.
Topf.—II. D. Vessel II.
Saure, ablauf = E. Acid outlet.
Topf.—I. = F. Vessel I.
Luft = G. Air inlet.
Kalorifer = H. Heater.
Trockenschacht = K. Drying chamber.
Cyclon = L. Cyclone separator.
Trocken zucker = M. Dry sugar.

Each of the arms of the tube can be heated to different temperatures, and connexion is provided between the arms. The distillate, containing hydrochloric acid, acetic acid and water, is introduced into one arm of the apparatus, which is kept at a temperature allowing only the hydrochloric acid to leave the tube in gaseous form, the water and the acetic acid being retained in the tube. We have succeeded in finding temperatures and concentrations at which practically the whole of the hydrochloric acid is driven off leaving the solution of acetic acid, water, and calcium chloride which flows over to the other arm of the tube. This arm of the apparatus is kept at a higher temperature, and causes the water and the acetic acid to evaporate. By means of this simple apparatus, which incidentally is continuous in operation, we are able to recover hydrochloric acid in the form of gas in the one arm of the tube and a vapour-mixture of water and acetic acid, free from hydrochloric acid, in the other. The acetic acid can be extracted from the vapours either by reaction with calcium or sodium carbonates or by using a concentration column if a highly concentrated acetic acid is required.

Our experience in working with materials capable of resisting hydrochloric acid aided us in developing useful forms of apparatus and heating arrangements for this process. This arrangement has a double advantage, for :—

(1) it allows the recovery of the acetic acid in a very pure form ; and
(2) it permits of the removal of a considerable quantity of water from the system.

This question is important because, during the washing of the lignin, a certain quantity of water has to be introduced into the process to avoid loss of hydrochloric acid. The retention of this water would cause the hydrochloric acid in the system to be diluted. Therefore, the water has to be removed, which is easily accomplished by this acetic acid recovery process.

The syrup from the distilling apparatus, containing about 55% to 65% of sugar, is dried by hot air in an apparatus shown in Fig. 5. I do not think I need to describe this apparatus in detail, the principle of which is common to various industries.

The syrup is injected together with compressed air through a nozzle. The hot air is blown into the shaft of the evaporator, whence the solid sugar, in finely divided form, enters a cyclone in which separation takes place : the dry sugar drops into the bottom of the cyclone separator, and is drawn off whilst the air containing water and hydrochloric acid gas leaving the plant is washed. The rest of the hydrochloric acid is recovered in an ordinary absorption plant.

The more or less diluted condensates and solutions of the hydrochloric acid are used in the same way as the distillate of the evaporation process, with the result that a very large percentage of the acid is recovered. Hydrochloric acid is lost only by retention of small quantities in the lignin and sugar. The lignin must be washed as free as possible from acid, so the loss is only about 5% of hydrochloric acid, calculated on the sugar produced, and the sugar itself contains about 2%.

The process is now a very simple one. The highly concentrated hydrochloric acid, which was regarded by most technical men as absolutely unworkable, has now become our obedient servant and behaves in quite an orderly way. Neither reaction vessels, pumps, conduits or buildings are attacked by the acid, nor are the workmen annoyed by acid vapours.

It took a vast amount of experimental work to find the right form of the apparatus and the proper construction materials. Such materials can be regarded as completely reliable only after having been used in the experimental station for at least one year. As a result of these experiments we now use in our plant many different kinds of special materials and combinations of materials to protect the metal parts against hydrochloric acid. The engineers, accustomed to handle steel, iron or other metals, had to change their methods of design and adapt themselves to completely different materials. It was not easy, for instance, at first to construct stone-ware pipe lines hundreds of metres long with hundreds of valves. To-day it is as simple a task as the construction of high-pressure-resisting joints and welded connexions which, twenty years ago when I began high-pressure work on a technical scale, was also a very difficult problem. A good deal of patience, money and confidence in the results are necessary to overcome the difficulties.

Before dealing with the products of the wood hydrolysis process, I want to mention some of the newer methods proposed for the production of sugar from wood. After the results of our process for treating wood with concentrated hydrochloric acid had become known, other methods were suggested.

Alexander Classen, whose process had been taken up by the Commercial Alcohol Company, divided the reaction between wood and hydrochloric acid into two parts. He obtained first a solution of cellulose and hydrochloric acid, separated this solution from the lignin and then conducted the saccharification with steam in a special apparatus. It seems that this process has not been worked on a large scale. I believe the reason is the difficulty in performing such a separation in a large apparatus.

Fredenhagen and Helferich used the reaction between cellulose or wood and hydrofluoric acid, which acts easily on wood and can be driven off by hot air after the reaction has taken place. It is certainly possible to produce sugar from wood by this process, but it might be difficult to work with hydrofluoric acid diluted by large quantities of air and avoid losses and attendant poisoning effects.

Schlubach showed that dry hydrochloric acid gas at high pressures has a similar effect to aqueous, highly concentrated, hydrochloric acid, so he proposed a process in which compressed hydrochloric acid gas is employed at from 40 atm. to 90 atm. It will be no easy task to build apparatus resisting hydrochloric acid gas when such high pressures are employed. Saccharification of wood always produces heat and the aqueous acid has the great advantage that it does not only act chemically, but is also a heat-regulating medium.

In treating wood with concentrated hydrochloric acid according to our process, the wood is converted into three components. As there is practically no loss, all the wood is recovered in usable form. The saccharification with dilute acids at high temperatures gives a much lower yield of sugar, because a considerable quantity is destroyed; further, the acetic acid cannot be recovered from very dilute solutions.

The lignin can be used directly for heating purposes in the process, and can be briquetted without the addition of a binder. Such briquettes have a calorific value of 5000 calories, or approximately 9000 B.Th.U., per lb. and form a clean and convenient household fuel. From these briquettes a pure and hard charcoal can be obtained. Under high pressure, the lignin can be pressed into hard and solid slabs, which can be sawn and drilled and may be used for different purposes.

The resins of the wood remain for the most part in the lignin. If desired they can be extracted in the normal way from the wood after it comes from the drier and before it is introduced into the diffusion battery.

There is not much to say about the acetic acid, which is recovered in a practically pure form.

The sugar, in the form in which it leaves the hot-air drier, contains about 2% of hydrochloric acid, a small percentage of inorganic compounds from the wood and some moisture. The content of reducing sugars is about 90%. Only a small part of the sugars is present in the monomeric form, the largest part being polymeric. According to the average molecular weight, the sugars seem to be tetrameric.

During the passage of the sugar from the battery to the atomizer, the percentage of tetrameric sugars is increased. The concentrated hydrochloric acid acts as a reverting medium for the primarily formed glucose, after the solution of the cellulose has taken place under the action of hydrochloric acid in the diffuser.

This polymeric sugar can easily and within a very short time be transformed into monomeric sugar by inverting it in a 20% solution a little above the boiling point. The small hydrochloric acid content in the sugar is sufficient for the inversion reaction.

Not only glucose, the product of the decomposition of the cellulose, is contained in the wood sugar, but also other forms of sugar, the quantity of which depends on the kind of wood treated. The sugar from conifers contains, besides glucose, especially mannose and pentoses; the sugar from foliaceous trees, chiefly pentoses in addition to glucose. Mannose and pentoses are the products of hydrolysis of the hemi-celluloses which can easily be extracted at relatively low temperatures from the wood by dilute acids. We have worked out a special process for this purpose. The hemi-celluloses are saccharified and extracted by treating the wood, before it is brought into the drier, with very dilute acid. The pre-extracted wood is then dried and brought into the battery. This process allows the recovery of pure xylose free from glucose in crystallized form. It is known that xylose can be consumed and digested by the diabetic, thus we are able to produce a relatively cheap form of nutrition for diabetics.

The raw sugar in its primary form can, after neutralizing, be used as a carbohydrate cattle food,

Experiments with this product have shown very good results, especially in fattening pigs. The nutritive value is practically the same as that of barley flour.

The raw product must undergo inversion before it can be fermented, but this inversion is a very simple and inexpensive process.

To produce alcohol, only the hexoses can be fermented, so that 100 kilos of reducing sugar yield about 52 litres of 100% alcohol; normal cane sugar yields about 60 litres. Other fermentation products, as for instance lactic acid, can also easily be produced from this product.

During recent years we have found a method for crystallizing pure glucose from the inverted solution of the raw sugar. This seemed a very difficult task in the beginning, and it took us a number of years to develop the crystallization process to its present simple form. The process is inexpensive, and no special or new technical devices are necessary to carry it out.

The crystallized glucose can be obtained either in an anhydrous form or containing water of crystallization. The product is chemically pure.

Having worked the wood hydrolysis process satisfactorily in large units, and having studied many different types of wood and waste wood, and solved the problem of good heat economy, we possess the fundamental knowledge for reliable calculation. In countries in which wood is obtainable in large quantities, for instance the Baltic States, Rumania, the north-west of the United States and Canada, wood sugar can be produced at a lower price than cane sugar is produced in the countries of the torrid zone. Also in England glucose can be produced at an extremely low price from imported wood.

The wood sugar represents not only a cattle food, but at the same time is a source for the production of yeast as well as of glucose for human consumption. Hence the fundamental elements for human food can be procured from raw materials of which Europe disposes in abundance.

For the over-populated industrialized European countries, therefore, the wood hydrolysis process may become an important factor towards independence of a food supply from abroad in the same way that the coal hydrogenation process will in some degree ensure independence of a foreign oil supply.

CANADIAN MINING

While no radium or uranium chemical products were commercially produced in Canada in 1932, Eldorado Gold Mines, Ltd. shipped hand-cobbed ore from its property at Great Bear Lake. This was consigned to the company's new radium-extraction plant located at Port Hope, Ontario, and this plant has already marketed finished products. Other mining operators in the Great Bear Lake district included Bear Exploration & Radium, Ltd., Consolidated Mining & Smelting Company of Canada, Ltd., and Great Bear Lake Mines, Ltd.

SOCIETY OF CHEMICAL INDUSTRY

OFFICIAL NOTICES

London Section. Members should note that the Joint Meeting with the Institution of Chemical Engineers, on Monday, Jan. 8, begins at 6 p.m. on this occasion.

Food Group. Change of Date. Members are asked to note that circumstances have arisen which make it impossible to hold the joint meeting with the British Association of Refrigeration on January 10, as arranged. Instead, it will take place at the Institution of Mechanical Engineers, Storey's Gate, S.W., at 8 p.m. on Wednesday, January 24. The subject "Refrigeration in the Food Industry" will be treated in four separate papers. Full particulars will be circulated.

BIRMINGHAM AND MIDLAND SECTION

The Birmingham and Midland Section of the Society of Chemical Industry held its first joint meeting with the Food Group on December 14. There was a good attendance of members.

By courtesy of the directors, a visit was paid in the afternoon to the Midland Counties Dairy, Corporation Street, Birmingham. The Section was honoured on this occasion by the presence of the President, Dr. J. T. Dunn.

The Midland Counties Dairy is one of the largest milk bottling depots in the Midlands and is capable of handling 12,000 gallons of milk per day. Two grades of milk are dealt with, "Grade A," which is pasteurized in a separate plant and then bottled, and the ordinary grade of milk which is sterilized at a high temperature in its own bottle. Some very interesting plant was the bottle washing machinery, which takes the greater part of the 30,000 gallons of water (supplied from the company's own artesian well) used daily. The washing, filling, and capping of the bottles is fully automatic and ingenious conveyors bring the crates of bottled milk to the decks for loading on to a fleet of horse, motor, electric, and hand-propelled delivery vans. Regular tests are made in the bacteriological laboratories on the milk supplied by the farmers, who receive bonus payments if their supplies attain fixed standards. It is significant that the percentage number of samples conforming to "Grade A" standards for bacteriological count and *Bacillus coli* content has risen from 77·25% in 1927 when the scheme was started to 92·28% in 1932.

The visitors were greatly impressed by the efficiency of the undertaking and the large extent to which use is made of mechanical equipment. They were afterwards entertained to tea and at the conclusion of the visit the President, on behalf of the Society, expressed his thanks to the Company for a most enjoyable afternoon.

In the evening Mr. H. W. Rowell presided at a joint meeting at the University of Birmingham, when Mr. A. W. Knapp (Chief Chemist, Cadbury Bros., Ltd.) read a paper on "Cacao Fermentation in West Africa."

The paper dealt mainly with the author's experiments and observations made on the Gold Coast and in Nigeria. These two British possessions produce more than half the world's cacao. All the cacao farms are owned and worked by natives. Manufacturers of cocoa and chocolate prefer cacao seeds which have been fermented as they produce cocoa and chocolate with a finer odour and a richer flavour than those which have been simply dried. Hence the farmer finds that fermented cacao is more easy to sell.

Although the word "fermentation" is correctly used in connexion with cacao to indicate a kind of spontaneous decomposition of the fruity pulp which surrounds the cacao seed when first taken from the pod, its use may easily convey a wrong impression, for the small amount of alcoholic liquid produced is not the object or end of the process, the alcoholic liquid being a by-product which at present runs to waste.

Mr. Knapp explained the necessary controls for scientific fermentation and then discussed in detail the native farmers' methods, including the use of the heap, the hole, and the various types of containers. Although fermentation proceeds somewhat more satisfactorily in the three-tier box arrangement, both the basket and the plantain stem frame proved satisfactory containers provided care was taken and the mass of fermenting seeds was given adequate mixing. Even the heap can be made to give a fairly good product provided it is mixed every two days.

The temperatures obtained in cacao fermentation in the heap are remarkably high, *e.g.*, on the second day 43° C. and on the third 50° C. or over. Three of the yeasts responsible, which have been isolated, have been found to have an optimum temperature of 40° C. Whether any of the acetic and lactic bacteria which occur in the later stages are impaired by a temperature above 45° C. is not known. When the heap is left unmixed it is liable on the fifth day to become mouldy for some depth from the surface. This growth has been shown by Bunting to be a mixture of a thermogenetic *Aspergillus* and a thermophyllic *Mucor*. This mould development is objectionable, particularly as Dade has shown that the mould penetrates the testa in front of the germ, and thus makes possible the moulding of the cacao by ordinary moulds which thrive under less humid conditions. By simply mixing once every two days, not only the risk of mould but also the production of a percentage of unfermented and germinated beans could be avoided. The author also discussed alternative methods to fermentation, and the effect of drying.

Illustrations to the lecture included a film.

Those taking part in the discussion were Mr. H. W. Rowell, Dr. L. H. Lampitt, Mr. Allen (Rowntree & Co.), Prof. R. H. Hopkins, and Mr. J. H. Alcock.

A hearty welcome was accorded by the Chairman to the President of the Society, who stated in reply that he was trying to visit every Section of the Society in the country during his term of office.

SOUTH WALES SECTION

An ordinary meeting of the South Wales section was held jointly with the local section of the Institute of Chemistry at Thomas' Café, Swansea, on Friday, December 8, Mr. E. E. Ayling, M.Sc., F.I.C., chairman of the latter section, being in the chair. A paper on "The Extraction and Refining of Paraffin Wax" was read by Mr. E. Thornton, B.Sc., A.I.C., A.M.Inst.P.T., of the National Oil Refineries, Neath.

The meeting was well attended and the lecture aroused considerable interest.

The paper dealt with the development of the processes for obtaining paraffin waxes from various sources and was intended to illustrate the application of scientific principles of control in the particular industry and the particular works with which the author is associated. The author said:

It must be admitted at the outset that the final word has not yet been said with regard to the chemistry of the process but that the experience gained is nevertheless valuable. Life's experience that fresh fruit and food are good was just as true and just as good science before the word "vitamins" was invented; similarly, the utility of controlled distillation and treatment to give the maximum yields of good wax is well established though the more detailed chemical and physical reasons for this still elude our search.

Historical.—Historically the process can be said to have begun with Dr. Young, who in 1850 patented a process for extracting paraffin wax from oil obtained from the shales of Scotland. Thus, it is essentially a British industry in origin though its practice is now world wide. The wax content of shale oils is about 13% but in modern crudes from which most of the wax for commerce is obtained to-day, the content varies from 5% to 15%, being less than 5% in most American crude oils, about 6% in Galician oils, 10% in various Burmah crudes and 13% or more in shale crudes.

Uses.—Paraffin waxes, as the name implies, are chemically inert and in addition are not miscible with water so that they find extended use in the waterproofing of paper, matches, etc. and in the preparation of polishes and insulating material, and also as non-conductors. The largest outlet is still the manufacture of candles, tapers, night-lights, etc., since the waxes are perhaps the only 100% ashless fuel in existence.

Constitution.—Chemically the waxes must be regarded as saturated hydrocarbons of the C_nH_{2n+2} type, where n will range from 20 to 30 in the chief marketed grades. The melting point ranges from 100° F. to 150° F. The composite solids having specified melting points probably have as marketed a considerably wider range of melting point, from 90° F. to at least 180° F. The boiling range of these waxes probably lies between 300° F. and 1000° F. at atmospheric pressure though they cannot be raised to temperatures much over 700° F. without decomposition.

It is probable that there are two main categories of paraffin wax, described by Dr. A. N. Sachanen, Miss L. G. Zherdeva, and A. N. Vasilyev (Nat. Pet. News, Apr. 22, 27, May 6, 13, 1931) as "ceresines" and "paraffins." *It is probable, though not proved, that the ceresenic type consists of side-chain isomers of the paraffins. The fact of the existence of these two kinds of waxes is of extreme importance to the refiner, though it is only slowly that the reason for his difficulties has become a little more clear.*

Extraction.—The method of obtaining wax from the crude could be divided into three main divisions, each capable of discussion at length, but which are briefly summarized as follows:

(1) Distillation.

(2) Extraction by pressing.

(3) De-oiling of the crude wax and removal of colour and odour.

(1) *Distillation.*—The first concentration of wax is achieved by distillation, selecting by means of boiling point a portion of the crude which will contain the waxes desired. This part of the process overlaps considerably with the preparation of lubricating oils, since the waxes are concentrated mainly in those fractions of the crude which are the source of lubricating oil. It would be necessary to remove the wax in any case in order to give lubricating oils which will flow freely at low temperatures and a considerable amount of dewaxing has no other object than this since the waxes extracted are rejected and burnt.

The concentration of wax in the press cuts may range from 5% to 15% and is obtained invariably by freezing out and removing the solid waxes in some manner. The waxes that can be worked up into commercial grades are contained in the lighter fractions of the lubricating oil base and can be removed by the simple process of freezing to the desired temperature, about 14° F., and filtering through suitable cloth in some type of industrial press.

The waxes contained in the heavier lubricating oils cannot be so easily removed as the crystal formation is not suitable for pressing. It is necessary in this case to dilute with some non-viscous solvent such as petrol, and either settle or centrifuge out the wax. Another process which also centrifuges the wax uses trichlorethylene as a solvent.

The kind of wax in the heavy fractions always retains oil very tenaciously and it is seldom that more than 70% recovery of oil can be obtained owing to the wax extracted retaining about its own volume of oil along with it.

For these reasons it is found that the amount of commercial wax that can be obtained is very much affected by the type of distillation employed and to-day pipestill and fractionating bubble column are rapidly displacing older equipment. The reason for this is that the presence of small quantities of high boiling material, probably ceresenic in character, in the cut which it is desired to press renders the pressing difficult and the subsequent refining operations more difficult still.

Distillation has therefore progressed successively through the stages of: (*a*) simple firing in a boiler without fractionating of the vapours; (*b*) controlled firing, *i.e.*, to give the minimum viscosity loss, but with the addition of a fractionating tower; (*c*) modern fully-controlled distillation with pipestill distillation and extremely good fractionating.

(2) *Extraction by pressing.*—The technique of extraction by pressing was very elaborate in the days when simpler forms of distillation were practised. The cut obtained was usually loaded with asphaltic, and what we should now call ceresenic bodies, which have a very deleterious effect upon the form of crystallization upon which the ease of pressing and the character of the crude wax obtained depend.

It was necessary to settle, to free from asphalt at about 110° F., to cool slowly in air, allowing still further heavy matter to drop out at about atmospheric temperature, and to follow this by cooling with brine at a temperature of about 10° F., before pumping through the presses. It was necessary also to re-press at about 1500 lb. pressure the first scales obtained, in order to squeeze out more oil before passing on to the sweating operation.

To-day with the more highly controlled distillation none of these operations is necessary. The press cut is taken as made, pumped through tubular coolers provided with scrapers and into the presses, a scale or crude wax being obtained having only about 15% oil content.

(3) *De-oiling of the crude wax and removal of colour and odour.*—The two processes just described have really been dewaxing the oil, *i.e.*, giving an oil as free as desired from wax content. From the wax point of view the next processes aim at the removal of the last traces of oil, colour, odour, etc. from the wax and the grading of the wax into definite melting point fractions. This is achieved by what is called sweating, which consists essentially of two steps: (*a*) cooling the molten wax carefully to form a crystalline mass of such a character that when re-warmed the successive stages of melting will have different melting points; (*b*) the careful re-warming of this mass and collecting into separate vessels of the successive drainings.

By this means "cores" are obtained of practically oil-free wax of reasonably narrow melting point, slightly coloured, having traces only of oil and a slight odour.

The last stage which consists in percolation through fuller's earth or roasted ore, such as bauxite, completely frees the wax from these undesirable properties and the wax thus freed is filtered finally through paper to remove all traces of filtering material and poured or moulded into slabs in which form the wax is marketed.

Throughout the whole of this process the microscope is of great value because there are peculiar

crystalline structures which render pressing and sweating easy and satisfactory, and these structures can be recognized under the microscope in a very definite manner.

A considerable amount of work has been done on the crystalline structure of paraffin waxes, but the only certain conclusion appears to be that they are of a fundamentally orthorhombic character with angles of 70 and 110. The final differences in assembly of the crystals which are of importance to the process technique are more a matter of size and method of growth than of the crystal properties of the fundamental crystal.

A long and interesting discussion followed and at the close a cordial vote of thanks was unanimously accorded the lecturer.

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BIOCHEMICAL SOCIETY

The 159th meeting of the Biochemical Society was held on December 15 in the Medical Lecture Theatre, St. Thomas's Hospital Medical School.

The following papers were read:

"The Distribution of Vitamin-*A* in the Organs of the Normal and Hypervitaminotic Rat," by A. W. Davies and T. Moore. Vitamin-*A* was assayed by the antimony trichloride method in the organs of rats which had received varying amounts of vitamin-*A* or carotene. Even when the liver reserves were quite low (100 b.u. per g.) small amounts of vitamin-*A* (5 b.u. per g.) were usually found in the kidneys, and often in the lungs. When large, but non-toxic, doses (5 mg. daily) of vitamin-*A* distillate were given to adult rats (1) the concentration of vitamin in the liver rose to extremely high levels (40,000 b.u. per g.), (2) the concentration in the lungs (500 b.u. per g.) was equal to that in the liver under normal conditions of nutrition (compare "normal" human liver reserve, 250 b.u. per g.), (3) the concentration in the kidney remained fairly low (50 b.u. per g.), (4) the concentration in other organs was extremely low except that occasional surprisingly high values were observed in the suprarenals (up to 1000 b.u. per g.). Even more massive doses of the distillate (12–14 mg. per day) given to young rats proved toxic, causing emaciation, hæmorrhagic rhinitis, loss of hair round the nose, and (1) in one rat, dying after 12 days, gross lung lesions, (2) in another rat, dying after 33 days, a peculiar softening and hollowing of the bones which had resulted in spontaneous fractures of the legs. The distribution of vitamin-*A* resembled that found in the rats given non-toxic doses except that the concentration in the lungs was even higher (1250 b.u. per g.), while in the rat dying after 33 days a high kidney value (625 b.u. per g.) was observed. Attempts to induce "hypervitaminosis A" by feeding carotene failed. On account of its limited solubility in fats only 8 mg. of the pigment could be given daily. Rats receiving this amount grew rapidly and remained in perfect health. On killing after 34 days the liver reserve was found to be only moderately high (1250 b.u. per g.), pointing to only about 1% absorption, as opposed to 15% in the case of vitamin-*A*. Only very small amounts of vitamin were present in the lungs, kidneys, and pancreas, negative results being obtained in all other organs. In general the kidneys and lungs appear to be the only organs other than the liver in which detectable amounts of vitamin-*A* are to be expected under normal conditions of nutrition.

"Diffusion of Various Sugars into the Yeast Cell," by H. Sobotka and M. F. Holzman. Observations on the influence of non-fermentable sugars on the fermentation of zymo-hexoses induced the authors to study the diffusion of various sugars into the yeast cell. Various types of yeast were mixed with solutions of various sugars. After thorough mixing, samples were centrifuged at once and after several intervals. The amounts of the carbohydrate remaining in the supernatant were analysed, and great differences in the amounts taken up by the yeast cells were observed. Xylose is taken up almost instantaneously, and reaches the same concentration in the cell fluid as without the cell. Galactose is absorbed at a slower rate: other sugars follow in a certain order. These experiments throw some light on the conditions observed in the fermentation of mixtures. They also allow an estimation of the intercellular, intracellular, and chemically bound water in yeast.

"A Note on the Influence of p_H on the Action of Hæmolytic Complement," by T. W. B. Osborn. By using buffer solutions isotonic with blood and of varying p_H the effect of the reaction of the medium upon the velocity of hæmolysis by complement was measured. The optimum was found to be in the region of p_H 7·5.

"The Estimation of Amino-acids in Wheat Flour," by L. W. Samuel (Introduced by A. G. Norman).—The technique of Brown (J. Bacteriology, 1923, **8**, 243) for the Sörensen formol titration was applied to the aqueous extract of wheat flour. When the titration was carried to p_H 8·0, before and after the addition of formaldehyde, no change in the amino

nitrogen content of the centrifuged extract was observed during several hours subsequent to separation from the flour.

When the titration was carried to p_H 9·0 before and after the addition of formaldehyde, one flour (a low grade) showed an increase in amino nitrogen with time of standing of the extract. Autolysis of a water suspension of this flour showed a greater increase in amino nitrogen content on titrating to p_H 9·0 than when titrating to p_H 8·0. Similarly, when taka-diastase was allowed to act on the gluten washed from this flour, there was a greater increase of amino nitrogen at p_H 9·0 than at p_H 8·0.

It is suggested that this phenomenon is due to the enzymic production of substances, containing carboxyl and amino groups, which have a low acid dissociation constant, and which do not become titratable even under the action of formaldehyde until p_H 9·0 is reached.

"Oxycholesterol," by O. Rosenheim and W. W. Starling. The name "oxycholesterol" was given by Lifschütz to a yellow resinous product obtained from cholesterol in various ways, which is characterised by a distinctive colour reaction. We have isolated from it, in small yields, a well crystallised unsaturated alcohol, melting point 236° (acetate m.p. 136°, benzoate m.p. 176°), which gives an intense Lifschütz reaction as well as the blue colour reactions with $AsCl_3$, trichloroacetic acid, etc., described since as characteristic for "oxycholesterol."

The clue to its constitution was afforded by the examination of the crystallised product obtained in good yield from cholesterol by the action of SeO_2 (Callow and Rosenheim, J. Chem. Soc., 1932, 387) which gives identical colour reactions. This substance, $C_{27}H_{46}O_2$, m.p. 176°, was found to be an unsaturated diol (dibromide m.p. 110°, monoacetate m.p. 191°, diacetate m.p. 169°). It did not react with the usual ketone reagents, but with 2 : 4-dinitrophenylhydrazine in acid alcoholic solution it yielded by an unusual reaction the 2 : 4-dinitrophenylhydrazone of cholestenone, m.p. 232°. On heating the diol with water in a sealed tube at 200°, cholestenone was obtained. The substance isolated from "oxycholesterol" gave the identical 2 : 4-dinitrophenylhydrazone.

The two substances are considered to be glycols, having the constitution $\Delta^{5,6}$ cholestene 3 : 4 diol. The fact that the α-diol, m.p. 176° has a lævorotation of $[\alpha]_D$ −60°, whilst the β-diol, m.p. 236° is dextrorotatory, $[\alpha]_D$ +8° suggests that they are cis-trans isomerides. The possible biological function of this reactive primary oxidation product as an intermediary in the transformation of cholesterol into bile acids and coprosterol was discussed.

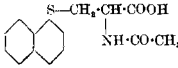
"Observations on the Metabolism of Naphthalene in Rabbits," by M. C. Bourne and L. Young. From the acidified urine of rabbits, feeding on oats and cabbage and receiving 2-gram doses of naphthalene dissolved in warm liquid paraffin, an organic, sulphur and nitrogen containing acid has been isolated by chloroform extraction and subsequent purification of the residue left after evaporation of the chloroform.

This compound is a water-insoluble, mono-carboxylic acid : melting point, 171·5° ; analysis (Schoeller) : carbon, 62·18% ; hydrogen, 5·30% ; sulphur, 11·24% ; nitrogen, 4·69%. The molecular weight, determined by the camphor method, was found to be 311 ; and the neutralisation equivalent found was 292. The empirical formula, calculated from the analysis is $C_{15}H_{15}SNO_3$.

On hydrolysis with boiling 12% H_2SO_4 one acetyl group was split off from the molecule. The de-acetylated compound was isolated, and was found to be an amphoteric substance with the characteristics of an amino acid. It had no definite melting point, but decomposed at 160°—165°C. Its analysis gave the following results: carbon, 63·15% : hydrogen, 5·36% : sulphur, 13·10% ; nitrogen, 5·44%. The empirical formula calculated from this analysis is $C_{13}H_{13}SNO_2$.

Hydrolysis of the parent substance with 6% NaOH resulted in the formation of ammonia and α-thionaphthol. The latter compound was identified by oxidising it (by aerating the alkaline solution after hydrolysis) to αα-dinaphthyldisulphide which was isolated. $C_{10}H_7·S·S·C_{10}H_7$ requires: carbon, 75·44% ; hydrogen, 4·43% ; sulphur, 20·15% ; found: carbon, 75·60% ; hydrogen, 4·26% ; sulphur, 20·17% (Schoeller). The αα-dinaphthyldisulphide melts at 91° (Leuckhardt) or 85° (Schertel) ; the melting point of the compound isolated was 89° C.

It is suggested that the compound, $C_{15}H_{15}SNO_3$, isolated from the urine of rabbits after naphthalene dosing, is α-naphthyl-mercapturic acid, a compound analogous to parabromphenylmercapturic acid (excreted after brombenzene feeding). The following constitutional formula is suggested :



"Some Observations on the Proteolytic Activity of the Gastric Juice in Anæmia," by W. J. Griffiths. Small amounts of a soluble, nitrogenous body are produced when muscle protein, precipitated at p_H 6·0 and washed with saline at the same reaction, is incubated with normal human gastric juice at p_H 6·0. This digestion is not due to pepsin or trypsin and is possibly of importance in view of Castle's work on the production, under similar conditions, of a principle capable of causing remission of symptoms in pernicious anæmia. In the few cases of pernicious anæmia so far studied this special proteolytic power of the gastric juice has been either much weaker or entirely absent.

"A Depressor Substance in Seminal Fluid," by M. W. Goldblatt. If the seminal fluid of man be centrifuged, the supernatant plasma is opalescent and alkaline in reaction. If the protein of the seminal

plasma be precipitated with alcohol or acetone a supernatant water-clear fluid is obtained. Removal of the alcohol or acetone at reduced pressure yields a turbid slightly-alkaline fluid which contains an extremely active depressor body or mixture of bodies. The depressor activity is demonstrable in the urethaned or etherised cat or rabbit, and persists even in the atropinised animal. This depressor activity remains after boiling in neutral solution or in $\frac{N}{2}$ acid but is rapidly destroyed on boiling in $\frac{N}{2}$ alkali. Some active material is adsorbed on the protein precipitate and may be removed by further extraction. The depressor-containing fluid also contains a substance (or substances) which produces a powerful contraction of the isolated rabbit intestine in oxygenate Tyrode solution, which persists even after atropinisation. The extracts also produce a powerful contraction of the isolated guinea-pig uterus. There is also present in these extracts a very active thrombokinase but this is present to a much greater extent in the alcoholic than in the acetone extract.

PERSONAL AND OTHER ITEMS

We regret to announce the death at the age of 56 of Sir Frank Baines, F.R.I.B.A., formerly the architect of the Office of Works. Sir Frank was responsible for many years for the construction of Government buildings of all kinds, and since leaving the official service in 1927 has been architectural and constructional consultant to Imperial Chemical Industries, Ltd., for the building of whose Millbank headquarters he was responsible.

Dr. Kräuzlein, Scientific Director of the Hoechst dye chemistry laboratory of I. G. Farbenindustrie, has been appointed an honorary doctor by Frankfort University in recognition of his inventive work on the chemistry of coal-tar colours, states *Die Chemische Fabrik*.

The death is announced at the age of 76 of Prof. H. E. Smith, who was for many years professor of chemistry and head of the medical school at Yale University.

Dyestuffs (Import Regulation) Bill

The Parliamentary Secretary to the Board of Trade, in moving the second reading of this Bill on Dec. 18, summarized the history of the British dyestuffs industry since the war, and stated that as there were in Europe producers of dyestuffs who could easily supply world requirements, it was essential that the present regulation of imports into Britain should be maintained to protect the home industry.

There were no other speeches in favour of the Bill. Representatives of the textile industry and other members opposed the Bill, stating that they would prefer a tariff on dyestuffs. The existence of an international cartel was deplored, and the question of Japanese competition was also raised. The Government spokesman in reply pointed out that cartels were not necessarily harmful, and that there was no evidence that dyestuffs would be cheaper if the British industry had not been developed. In Japan there was no selling of dyestuffs likely to compete.

The second reading was carried by 245 votes to 72.

British Standard Specifications

The British Standards Institution has issued the following specifications:

Crude carbolic acid 60's and 45's (515—1933) *and distilled carbolic acid 60's and 45's* (516—1933).—The specifications prescribe limits for specific gravity and crystallizing point of the products, and for percentages of water, non-volatile residue, neutral oils and pyridine bases, and acid or alkali.

Phenol (523—1933).—The standard properties are solubility in water, absence of non-volatile residue, crystallizing point, and boiling point.

Cresylic acid of high orthocresol content (517—1933); *cresylic acid, 50/55% metacresol* (521—1933): *refined cresylic acid, grades A and B* (524—1933).—Following a general description, limits are prescribed for water content, specific gravity, temperature of distillation, and content of neutral oils and pyridine bases, acid or alkali, and H_2S. In addition a content of orthocresol is specified in No. 517 and of metacresol in No. 521.

Orthocresol, metacresol, and paracresol (522—1933).—For each substance are prescribed solubility in alkali, maximum residue on evaporation, crystallizing point, and boiling point; for metacresol specific gravity limits also are indicated.

In each specification methods of making the necessary determinations are described. Specifications for thermometers, hydrometers, and glassware are included where the use of these is involved.

Copies of the specifications can be obtained from the British Standards Institution, 28, Victoria Street, London, S.W.1, price by post 2s. 2d. each.

International Tin Cartel

The French Minister of Commerce has announced that France is joining the International Tin Cartel, which has agreed to increase the tin production of French Indo-China by 300% within the next 3 years. The estimated production for 1933 is 1000 tons; the quota has been fixed at 1700 tons, 2500 tons, and 3000 tons for the three next following years.

Canadian Duties on Tinplate

The Canadian Tariff Board has decided that "dumping duties" should no longer be chargeable on tinplate imported from the U.S., as tinplate has not been produced in Canada since last May. The fact that a small branch plant of Richard Thomas & Co. has recently started to produce tinplate in Ontario is ignored by the Board. The National Revenue Department, which has disagreed with the

Tariff Board on other matters, may decide not to act on the decision.

Shrinkage-Proof Cloth

An announcement has been made by the Bradford Dyers' Association concerning the recently invented "Rigmel" process for producing cotton and other cloth which will not shrink when washed. The "Rigmel" machine includes an arrangement of rollers which compress the fabric by an amount varying up to 14% of the length, so that tension in it is removed. The B.D.A. has made an agreement with the Cluett Peabody Co. of New York, which is interested in a similar device, concerning the manufacture of both machines. It is felt in Lancashire that although the new process, which necessarily involves an addition of 1d. or 2d. a yard to the price of the cloth, cannot solve the problems of diminished export trade, it will influence the demand for good quality textiles as trade improves. The process has been successfully applied to linen as well as cotton, and its application to wool is being considered.

Chemical Engineering Equipment Institute

This newly formed United States organization has now launched a broad programme aiming at self-government of the industry, and has submitted a code of fair competition to the N.R.A. At the annual meeting the Institute elected Mr. J. V. N. Dorr, president of the Dorr Co., Inc., as president and Mr. H. D. Miles of the Buffalo Foundry & Machine Co. as vice-president.

German Gasholder Explosion

The Institution of Gas Engineers has issued a report on the serious explosion of a gasholder of the waterless type which occurred at Neunkirchen, Germany, last year. This shows that the primary cause of the disaster was the use by a workman of an oxy-acetylene torch when working on a by-pass main in the vicinity of the holder. Gas had apparently leaked into this and caused a minor explosion which damaged a valve at the end of the by-pass, allowing flames to spread up the outside of the holder. The explosion of the holder which followed was due to the expansion by outside heat of its side sheeting, and not to any defect in the gas-tight fitting of the piston within it. It is considered that the precautions taken in this country when undertaking repairs in connexion with waterless or other gasholders are sufficient to prevent the possibility of an explosion of this kind.

Organization of Photographic Industry in Germany

The newly formed Association of German Photographical Manufacturers, which exists to co-ordinate and protect the activities of the whole industry, has recently appointed as its president Herr M. Mayerhofer, of the firm of Otto Perutz, Munich, his deputies being Herr R. Schafer of Zeiss-Ikon and Herr B. Uhl of I. G. Farbenindustrie. The wide ramifications of the photographic industry have necessitated division into seven groups, each consisting of a number of firms and in charge of a head who is responsible to the president. The groups are: photographic chemicals; films; laboratory and developing apparatus, etc.; plates; paper; cameras; kinematograph apparatus.

Alcohol in Flavouring Essences

Small bottles of rum, brandy, and other flavouring essences on sale in unlimited quantities at a multiple store, and alleged to contain 90% of ethyl alcohol, were the subject of a recent Parliamentary question. The Financial Secretary to the Treasury stated in reply that these essences had been analysed and found to contain no ethyl alcohol, but a proportion of *iso*propyl alcohol, on the sale of which there was no restriction.

British Pharmaceutical Codex

The Pharmaceutical Society has recently issued a booklet summarizing the more important dressings for which revised requirements will be prescribed in the next issue of the B.P. Codex. This includes standards for a number of gauzes, wools, bandages, etc., and instructions for analytical determinations.

There have also been issued a summary of standards for crude vegetable drugs to be included in the new Codex, a similar summary of new or revised formulæ, and another dealing with sera, vaccines, vitamin concentrates, etc.

The four booklets can be obtained from The Pharmaceutical Press, 23, Bloomsbury Square, London, W.C.1, price 1s. 6d., 2s., 2s. 6d. and 1s. 6d. respectively. The Editor invites comments on the proposed standards.

Industries of the Bombay Presidency

The *Indian Trade Journal* gives the following information, from the Annual Report of the Department of Industries:

The production of soap in the Bombay Presidency has increased considerably during the year, a number of new unregistered companies having been started. Imports of soap were one-third less than during the previous year, while imports of caustic soda, chiefly used for soap-making, show a substantial increase.

During the year new factories have been established in the Presidency for the production of non-ferrous alloys, Bakelite materials (2), razor blades, silk fabrics (2), dry cells, and fireworks.

Artificial Indigo Production in Japan

A report from the Japanese Department of Commerce states that the production of artificial indigo in that country is now nearly sufficient for the demands of the domestic textile industry. The value of the output of this product has risen from 134,000 yen during the whole of 1929 to 1,045,000 yen during the first six months of the present year, while the value of imports fell from 2,000,000 yen to 30,000 yen during this period. The two largest manufacturers of artificial indigo in Japan have recently enlarged their plant.